Evaluation of Small Arms Range Soils for Metal Contamination and Lead Bioavailability

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Although small arms ranges are known to be contaminated with lead, the full extent of metal contamination has not been described, nor has the oral bioavailability of lead in these soils. In this work, soil samples from ranges with diverse geochemical backgrounds were sieved to <250 μm and analyzed for total metal content. Soils had consistently high levels of lead and copper, ranging from 4549 to 24 484 μg/g and 223 to 2936 μg/g, respectively, while arsenic, antimony, nickel, and zinc concentrations were 100-fold lower. For lead bioavailability measurements, two widely accepted methods were used: an in vivo juvenile swine relative bioavailability method measuring lead absorption from ingested soils relative to equivalent lead acetate concentrations and an in vitro bioaccessibility procedure which measured acid-extractable lead as a percent of total lead in the soil. For eight samples, the mean relative bioavailability and bioaccessibility of lead for the eight soils was about 100% (108 $\pm$ 18% and 95 $\pm$ 6%, respectively) showing good agreement between both methods. Risk assessment and/or remediation of small arms ranges should therefore assume high bioavailability of lead.

Introduction

The annual utilization of lead by humans in the United States varies between 1.4 and 1.5 million metric tons (*1*) representing over 4.5 kg (10 pounds) of lead per person per year. Storage batteries consume 80% of this total, while ammunition accounts for about 4%, or 60 000 t of lead. While recycling of batteries ensures that some 1.1 million metric tons of lead are reused annually (*1*), lead bullets ultimately end up in soil on the estimated 3000 small-arms ranges (SAR) used by the Department of Defense (DoD) or the other 9000 nonmilitary ranges thought to be in use (*2*). For the DoD, Federal Agencies, and State bodies, these SAR soils represent significant efforts in stewardship, environmental risk assessment, and remediation, so that training of personnel and future land use can be reconciled.

Lead from ammunition can be present in the form of lead shot, copper jacketed bullets (80% lead), or to a lesser extent in lead-based compounds used as primers (*3*). At the berms, or backstops, of small-arms ranges three general phases of Pb can exist: the first is when spent copper-jacketed bullets in the soil remain relatively intact and contain metallic Pb; the second when bullets fragment upon impact into very small Pb particles; the third where physical and chemical weathering over time generates oxidized forms of Pb (*4, 5*) such as lead carbonate or lead oxide. Though a range of metals, including lead, copper, antimony, arsenic, and zinc are used in the manufacture of bullets: lead, because of its overwhelming concentration mass and toxicology, is the predominant driver of risk at ranges.

At DoD sites that contain SARs, human health risk assessments are carried out on a case by case basis with subsequent outcomes compared with future land use scenarios, such as ongoing range operation, residential, or brownfield sites. In accordance with U.S. Environmental Protection Agency (EPA) methods, risks from lead in a residential setting are evaluated using the integrated exposure uptake biokinetic (IEUBK) model (*6*) which is used to predict blood lead distributions based on environmental exposures. One of the important input terms in the IEUBK model is the absorption factor for lead in soil and dust. The default value is 30% (which is a product of the absolute and relative bioavailability of lead acetate in children; 0.5 $\times$ 0.6). Thus the relative bioavailability of lead in soil is assumed to have a default value of 60%. EPA recognizes that this value may vary from site to site and encourages the measurement and use of site-specific bioavailability factors for lead, using the in vivo swine model (*7*).

Site specific in vivo lead bioavailability testing has concentrated on mining waste (*8, 9*) and treatment strategies. However, the diverse locations of small arms ranges, with soils that can vary from acid to neutral and from sandy to clay-rich, raises the question of whether different bioavailability values could exist across different ranges. Previous studies of ranges have concentrated mainly on the extent of lead contamination (*10*), mobility of lead (*4*) and lead ecotoxicology (*11, 12*), but little effort has been made to establish the potential human bioavailability of lead in these soils using in vivo models, or the extent of other metal contamination. In this paper a qualitative and quantitative assessment of metals in the soil fraction <250 μm was carried out in a wide variety of SAR soils; followed by measurements of the oral relative bioavailability of SAR soil lead using both the juvenile swine in vivo oral bioavailability method (*13, 14*) and an in vitro bioaccessibility (IVBA) method (*14, 15*).

Materials and Methods

While a total of 24 soils were screened using the low-cost in vitro method, only eight were selected for in vivo analysis. Selection was based on including as wide a geographical/geochemical spectrum as possible, rather than a range of concentrations; this was because during the early part of the study in vitro screening of samples showed consistently high bioaccessibility measurements regardless of concentration (see Supporting Information (SI) Figure S1) and assessing the impact of other soil properties on in vivo RBA was also important. Samples came from a variety of soil types, from eight different states including Maryland (MD1 and MD2), Alaska (AK), Louisiana (LA), Nebraska (NE), Oregon (OR), Washington (WA), and South Dakota (SD). Soil properties varied, including soils with high organic matter, low pH, and high cation-exchange capacity. For each site, composite samples were taken by scooping the top few inches of soil from approximately five or more subareas of the berms where areas of high lead had been identified. For identification of

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TABLE 1. Total Metal Concentrations and Soil Characteristics in Small Arms Range Soils from Across the U.S.[a]

	MD1	MD2	LA	AK	NE	WA	SD	OR
Fe	14,999 ± 436	8,389 ± 124	18,106 ± 542	26,069 ± 281	17,877 ± 341	27,576 ± 891	30,967 ± 775	36,604 ± 621
Pb	14,847 ± 193	19,906 ± 371	16,775 ± 571	13,670 ± 151	15,416 ± 593	24,484 ± 738	4,549 ± 181	19,800 ± 32
Cu	1,419 ± 31	1,727 ± 35	909 ± 72	796 ± 14	904 ± 63	2,080 ± 129	223 ± 21	2,936 ± 66
Ti	176 ± 2.3	70 ± 1.3	225 ± 1.4	716 ± 7.5	452 ± 3.8	1709 ± 9.5	312 ± 15.1	2262 ± 17.2
Zn	205 ± 4.3	157 ± 1.6	208 ± 5.2	153 ± 2.5	170 ± 8.7	284 ± 11	112 ± 3.8	102 ± 9
Si	523 ± 39	430 ± 110	687 ± 74.2	328 ± 42	758 ± 96	537 ± 22	693 ± 66	508 ± 7.1
Mn	102 ± 2	83 ± 1	342 ± 2	216 ± 2	458 ± 5	408 ± 4	930 ± 12	592 ± 4
Sb	33 ± 0.5	91 ± 1.1	42 ± 1.0	51 ± 1.0	41 ± 1.1	33 ± 0.9	7 ± 0.2	54 ± 0.5
Ni	6 ± 0.1	3 ± 0.1	15 ± 0.2	7 ± 0.9	3 ± 0.3	247 ± 3.3	48 ± 1.0	102 ± 1.0
Zr	8 ± 0.1	3 ± 5.0	12 ± 0.1	2 ± 0.03	19 ± 0.1	14 ± 0.1	24 ± 0.5	33 ± 0.7
As	3.6 ± 0.1	2.8 ± 0.3	10.9 ± 0.16	27.9 ± 1.0	16.6 ± 0.5	6.4 ± 0.3	16.0 ± 0.2	11.7 ± 0.4
pH	6.27	6.11	7.75	4.4	8.15	7.44	8.19	7.02
CEC	0.95	1.1	12.43	13.36	17.1	4.09	28.62	8.04
TOC	0.518	1.966	0.853	31.63	0.832	1.36	2.458	1.19

[a] Abbreviations: Ti = titanium, Fe = iron, Ni = nickel, Zr = zirconium, Pb = lead, Cu = copper, Mn = manganese, Si = silicon, Zn = zinc, As = arsenic, Cd = cadmium, CEC cation exchange capacity, TOC = total organic carbon. Values are mean of three to five subsamples taken from soil samples that had been sieved to <250 micrometer. Metal concentrations determined by ICP-MS. Metals in μg/g. TOC as %. CEC in meq/100 g.

high lead areas, the Innov-X environmental analyzer, a handheld nonradioactive XRF (Innov-X Systems, Inc., MA) was used to locate hotspots. Soils were air-dried to a final soil moisture content of approximately 4%, and then sieved through an ASTM no. 10 (2000 μm) and no. 60 (250 μm) sieve according to EPA protocols (*14*). Dried and sieved samples were stored in Nalgene containers. Before subsampling, soils were well mixed to eliminate any settling of particles during storage. Total metal analysis was carried out using nitric acid/hydrofluoric acid digestion followed by inductively coupled plasma−mass spectrometry (ICP-MS).

In vitro bioaccessibility analysis was carried out using a well established method (*15*) which has been approved by EPA for evaluation of the bioavailability of lead in soils (*14*). Briefly, triplicate 1.00 g subsamples of test soil were taken from each well-mixed sieved soil, and each 1.00 g sample was extracted in 100 mL of 0.4 M glycine (tissue culture grade, Fisher Scientific Limited, PA) buffered solution, which was adjusted to pH 1.5 using trace-metal grade (Fisher Scientific Limited, PA) HCl, in 125 mL Nalgene bottles. The closed bottles were placed in a heated extraction device and rotated end-over-end for 60 min at 37 °C. A 10 mL aliquot of solution was then removed, filtered through a 0.45 μ cellulose acetate filter (BioExpress, UT) and analyzed for lead following EPA method 6020A (*16*) on a Varian ULTRAMASS ICP-MS (Varian, Inc., CA). Bioaccessibility was expressed as the ratio of extracted lead to the total lead in the sample, where total lead was measured using hot nitric-hydrochoric-hydrofluoric acid digestion followed by ICP-MS analysis using EPA method 6020A (*16*). Electron microprobe analysis (EMPA), using a JEOL 8600 electron microprobe, was used to identify and count lead particles (*17*); backscatter imaging was used to examine Pb bearing particles. Total organic carbon was measured on a COSTEC 4010 CHNS analyzer. Other measures of soil properties, including pH (U.S. EPA SW-846−9045D), cation-exchange capacity (CEC) (*18*) and total organic carbon (TOC) analyses were carried out.

In vivo lead RBA analysis was carried out using a previously published method described in detail elsewhere (*13, 14, 19*). In brief, lead RBA in juvenile swine was determined by comparing the systemic absorption of lead from oral ingestion of soil compared to that of lead acetate. Groups of five juvenile swine were dosed twice-daily (0900 and 1500 h) for 14 continuous days via doughballs containing either the test material (a SAR soil) or a lead acetate solution. Due to space constraints of the animal laboratory, in vivo RBA tests were carried out in a series of studies: Study 1 = MD1 and MD2 materials; Study 2 = AK and LA; Study 3 = NE and OR; Study 4 = WA and SD. Each study included lead acetate dose groups (three dose levels per study), a negative control dose group (three animals per study) and groups of test material dose groups (three dose levels per test material per study). Venous blood samples were sequentially drawn into EDTA Vacutainers (Becton Dickenson Company, Franklin Lakes, NJ) on days 0, 3, 5, 7, 9, 12, and 15 of the study, and liver, kidney, and femur samples were collected at terminal necropsy (day 15 of each study). Lead analysis of blood and tissue samples were determined following methods described previously (*13, 14, 20, 21*); samples were analyzed by a Perkin-Elmer 800 graphite furnace atomic absorption spectrometer. Lead analysis adhered to recommended quality assurance procedures for lead using Centers for Disease Control reference blood samples, National Research Council Canada DOLT-3 dogfish liver, National Institute of Standards and Technology Standard Reference Material 1400 (bone ash), duplicates, and periodic calibration checks and blanks. Performance standards for quality control data were within prescribed limits.

Data reduction was carried out as detailed by the U.S. EPA (*21*). For blood, plots of blood lead concentration versus time were used to calculate the area under the curve (AUC) for each dosed animal. The, a plot of AUC vs administered dose was used to characterize the dose response curves for each group. For liver, kidney, and bone, the dose response curve was based on the tissue concentration measured at sacrifice versus the administered dose. The blood lead dose response curves were fit to a nonlinear model, whereas liver, kidney, and bone were fit to linear models:

$$\text{blood lead AUC: } y = a + bx[1-\exp(-cx)]$$
$$\text{liver, kidney, bone: } y = a + bx$$

In all cases, fitting of the models to the data was performed using simultaneous weighted regression (see U.S. EPA (*21*) Appendix D for details). The relative bioavailability of lead was then estimated using the ratio of the model slope parameters (b) for test material (lead in soil) to the reference material. The uncertainty bounds around the point estimate of RBA for each tissue and for all tissues combined were calculated using Fieller's Theorum (*21*). All animal protocols were approved by the University of Missouri Institute Animal Care and Use Committee.

Results and Discussion

Comprehensive metal analyses of the eight study soils (the fraction <250 μm) along with general soil characteristics (pH, TOC, and CEC) are shown in Table 1. The concentrations of

lead rivaled and even exceeded those of naturally occurring iron in the soils, ranging from 4549 to 24 484 μg/g Pb. Lead and copper tracked each other in concentration across soils (Table 1), with copper about 10-fold less than Pb, ranging from 223 to 2936 μg/g. Other elements such as arsenic, antimony, nickel, and zirconium were found at significantly lower levels than either lead or copper. Cadmium concentrations were below background while tungsten was not detected (data not shown). Although no standard textural analyses was conducted on the soils, each was provided with a general descriptor, as follows; MD 1 and MD2 (sandy), AK, OR, and WA (organic), LA, NE, and SD (clay). Soil pH varied; ranging from moderately alkaline (NE, SD), slightly alkaline (WA, LA), and neutral (OR), slightly acidic (MD1 and MD2), to extremely acidic (AK) in the organic peaty soil. Cation-exchange capacities (CEC) ranged from 0.95 to 28.6 meq/100 g and corresponded well with the general textural classifications, with the higher values associated with clay-rich soils (SD, NE) and the low values indicative of sandy soils (MD1, MD2). Organic carbon was highest in the peaty soil from Alaska and lowest in the sandy soil from Maryland.

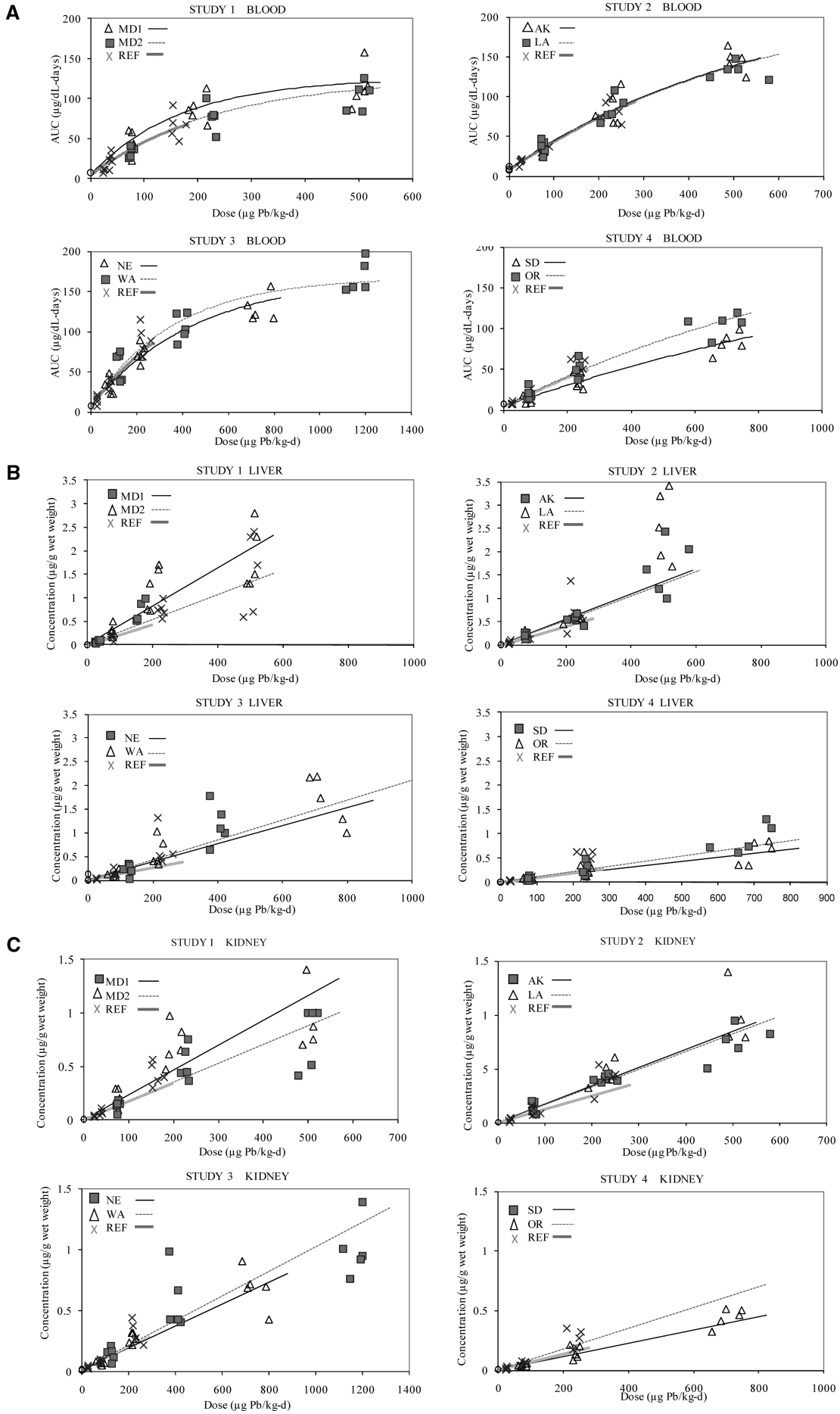
The primary constituents of munitions in small arms firing ranges (50 caliber or less) are lead (projectile), antimony (alloy with Pb), arsenic (increases hardness), tin (alloy with Pb), copper (bullet jackets), zinc (jacket alloy metal), and iron (tips on penetrator rounds) (*2*). The bulk of the bullet mass consists of Pb (∼80%) and Cu (∼20%) and this was reflected in the 100-fold greater concentrations of these metals over other elements in the soils. Other elements that could erode from bullets, such as nickel, antimony, zinc, and arsenic were found at significantly lower concentrations. Arsenic levels, though low, could possibly be from arsenic that had been added in small quantities to lead as a hardening agent. Tungsten was not found in any of the eight samples; there are only a few ranges where tungsten-nylon bullets have been tested. Overall, the presence of high concentrations of lead and copper, and the significantly lower concentrations of other metals, indicates that these two metals are justified as the primary concern at small arms ranges.

For analysis of the in vivo data, the measured lead values in blood, liver, kidney, and bone were modeled by fitting dose−response curves for each tissue and calculating the ratio of the slopes (*13*). Figure A−D shows the dose−response curves for blood (AUC vs μg Pb/kg-day), liver (μg/g wet weight), kidney (μg/g wet weight), and bone (μg/g dry ash residue) for each of the eight soils, as well as the reference material (lead acetate) and the fitted lines for each soil; Supporting Information (SI) Table S1 shows the model estimates. There was virtually no difference in blood or tissue levels between the reference material and the test materials as seen in Figures A−D. For both types of materials, blood lead levels started out below detection limits (∼1 μg/dL) on day 0, then rose to a near steady-state in about 7−10 days. Blood level response was typically nonlinear (Figure A) but was approximately linear for liver, kidney, and bone lead (Figure B−D). Variability in response was higher in kidney and liver than for blood and femur measures and tended to increase as the dose increased. A similar pattern of increasing variability with increasing dose has been well-documented (*6*) and is accounted for in the model-fitting procedure by the use of weighted least-squares regression. The negative controls (food without small arms range soil) were below detection limit and are not visible on the plots. Summary results and 90% confidence intervals are shown in Table 2. In vivo RBA estimates were high for all soils, with confidence intervals that included 100% in all cases (Table 2). The actual Pb values used for dosing animals are listed in Table 2 and differ (within an acceptable range) from the values in Table 1 because the latter analysis was carried out on samples after the in vivo work was carried out.

For the in vitro method, samples were analyzed in triplicate and the results for the eight selected study soils are listed in Table 2, along with the final in vivo results for comparison. As indicated, in vitro bioavailability was also high for all soils, exceeding 90% in seven of eight cases. A total of 24 samples was collected and analyzed using the in vitro assay during the course of this study, and results for all 24 samples (SI Figure S1) show that this method is reliable over a broad range of concentrations; with mean Pb bioaccessibility in these soils being 91 ± 11%. Electron microprobe speciation techniques showed that the predominant forms of Pb were oxides and carbonates, compounds known to have high bioavailability (SI Figure S2) while an electron micrograph of a lead particle from a sample shows native (metallic) lead surrounded by rinds of oxide and carbonate (SI Figure S3). Finally, to compare in vitro/in vivo results of this study to bioavailability from other types of lead-contaminated soils these data were plotted along with the validation data of Drexler and Brattin, 2007 (SI Figure S4). The results show that the bioavailability of SAR soils falls at the high end when compared to soils from other types of sites.

The consistently high bioavailability and bioaccessibility observed in all sampled soils seemed to be independent of soil properties such as pH, organic carbon, and CEC; indicating that at these Pb levels, soil properties do not influence bioavailability, though the sample size was small. The predominance of lead carbonates and oxides in the soils (SI Figure S2) is consistent with the highly oxidizing conditions found in raised berms. However, some berms can have lower lying waterlogged areas which could result in anerobic conditions; but these also had high bioaccessibility when measured using the in vitro method (data not shown). For a few samples in this study (MD1 and AK), the measured in vivo RBA was slightly greater than 100%. Although the true RBA of test materials should never exceed 100%, measurement error (e.g., dosing errors, analytical instrument variation, etc.) can result in a measured RBA value slightly above or below the true RBA. The effect of measurement error on the measured RBA is captured in part by the uncertainty bounds associated with each point estimate, and in all cases, the uncertainty bounds bracket 100% bioavailability. Thus, the interpretation of the in vivo RBA estimates should be that the SAR soils are highly bioavailable to the point that they are not functionally different than the lead acetate reference material.

There are no known instances of acute lead poisoning of humans from SAR soils. Humans generally are more at risk in indoor ranges, where poor ventilation and repeated inhalation exposure can increase blood leads in firearms instructors, though in general the risk is low (*22*). Ranges are usually located in remote areas so that civilian exposure to lead is unlikely while exposure of soldiers during target practice is low. Bovine calves have been poisoned (blood lead 94 μg/dL) due to grazing at the target area of a small arms range (*23*) whereas woodchucks resident at small arms ranges were not found to have elevated blood lead levels (*12*). Songbirds could be at increased risk at ranges (*24*) though sampling of adults and nestlings from ranges has showed subclinical levels of lead in blood (*25*). In spite of these equivocal results, SARs represent a large burden of metal contaminated sites for DoD management, and research continues to focus on control and remediation of existing sites. Guidance for the management and/or remediation of open and closed ranges is available (*2*), and immobilization strategies involving phosphate have been used during remediation (*3, 26*). Though phosphate amendments have been reported to stabilize Pb and reduce bioavailability, there is a need for long-term confirmatory studies of reduced bioavailability.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STUDY 2 BLOOD
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Dose (µg Pb/kg-d)
STUDY 3 BLOOD
NE
WA
REF
AUC (µg/dL-days)
Dose (µg Pb/kg-d)
STUDY 4 BLOOD
SD
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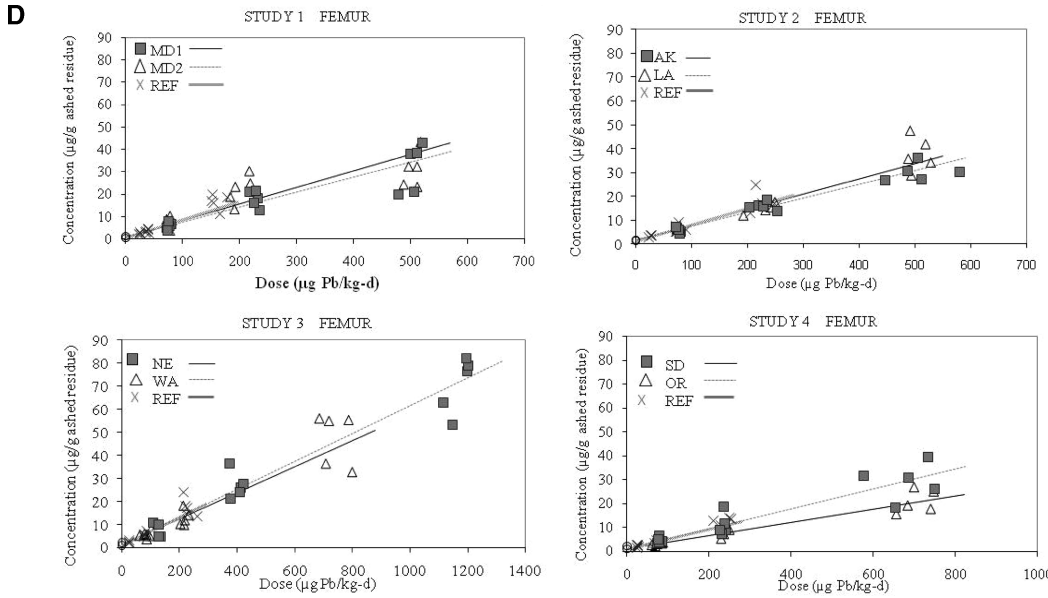

FIGURE 1A−D. Dose response curves for blood, liver, kidney, and bone after 14 day daily exposure of swine to lead in small arms range soils. Each graph represents testing of two soils, as indicated. The symbol "x" indicates lead acetate reference material which was used as a reference to calculate relative bioavailability. Where visible the lead acetate fitted line is denoted by a shaded solid line. Blood AUC values were calculated from graphs of daily blood levels over 15 days. Liver, kidney, and brain were calculated from tissues taken at necropsy. Negative controls, which were less than background, are not shown.

TABLE 2. Lead Value Used for the in Vivo Study and the Results for the in Vitro and in Vivo Assays[a]

site	lead (mg/kg)	in vitro (%)	in vivo (%)
MD1	15 667	94 ± 2	140 (80−218)
MD2	23 333	98 ± 2	103 (69−142)
AK	13 992	93 ± 2	116 (86−160)
LA	15 705	90 ± 2	112 (79−155)
NE	14 372	100 ± 3	93 (59−153)
OR	19 464	100 ± 2	112 (81−151)
WA	23 409	83 ± 1	107 (67−155)
SD	4503	99 ± 1	77 (55−108)

[a] In vitro assay is mean and standard deviation of measurements. In vivo assays include the 90% confidence interval.

This work has provided a qualitative and quantitative examination of metals in small arms ranges soils, followed by measurements of bioavailability using two established methods. The predominant metals in a study of eight small arms range soils from diverse regions of the U.S. were lead and copper with other metals at significantly lower concentrations. The relative bioavailability of lead at these ranges was 100%, whether measured by an in vivo or in vitro method. Risk assessment and/or remediation of small arms ranges should therefore assume a high relative bioavailability of lead.

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Supporting Information Available

Additional figures for in vitro and in vivo data, speciation analysis, and electron microprobe of particles are also presented as well as a table with model parameters. This material is available free of charge via the Internet at http://pubs.acs.org

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